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1. Untranslatable words are replaced with asterisks (****).
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Translated: 17:04:57 JST 03/23/2005

Dictionary: Last updated 10/12/2004 / Priority:

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[Claim(s)]

[Claim 1] (A) The metal-containing fire retardancy catalyst which are rubber denaturation styrene resin, (B) polyphenylene ether, the (C) metal oxide, and/or a metal powder, the (D) organic phosphorous compound, and the styrene resin composition characterized by consisting of a (E) triazine frame content compound.

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the resin composition object excellent in fire retardancy. Furthermore, it is related with the fire-resistant shock resistance styrene resin composition which does not contain a halogenated compound in detail.

[0002]

[Description of the Prior Art] Since the rubber denaturation vinyl aromatic series resin represented by HIPS is excellent in shock resistance, rigidity, and electric insulation in addition to excelling in a moldability and dimensional stability, it has come to be used in many fields including household appliance parts and OA equipment parts. To the plastic material used in this field, from the problem of safety, the fire-resistant demand is increasing and various fire-resistant specification is defined in recent years. Although various methods are devised as a method of giving fire retardancy to the resin which ***** requires, very generally halogenated compounds, such as a high bromine compound of a fire-resistant effect, and the method of adding antimony oxide to resin if needed are adopted. Although nucleus bromination aromatic compounds, such as deca promo diphenyl ether, tetra-promo bisphenol A, and a bromine-ized phthalimide, are known as a bromine compound Although the outstanding fire retardancy was acquired, impact strength and heat deflection temperature fell, depending on the case, the flame retarder carried out PURIDO out of the method of depending on addition of these flame retarders to the mold-goods surface of resin, and it had the problem of worsening mold-goods appearance. Furthermore, at the time of shaping of resin, by the pyrolysis of the halogenated compound, poisonous gas was generated on the human body, and it had the problem of corroding metal mold and a screw again.

[0003] For this reason, the method of fire-retardancy-izing without using a halogenated compound is examined. Although the method of adding hydrated metallic compounds, such as an aluminum hydroxide and a magnesium hydroxide, to resin was known as this method, in order to acquire sufficient fire retardancy, the above-mentioned hydrated metallic compound needed to be added so much, and it had the fault that the property of resin original was lost.

[0004] As a method of on the other hand not using such a hydrated metallic compound, vinyl aromatic series resin, The flame-retardant-resin constituent (JP,S54-38348,A, JP,S54-38349,A, the Europe patent No. 311,909 Description) which consists of a nitrogen-containing compound chosen from polyphenylene ether, an organic phosphorous compound, triazine, and/or its derivative is indicated. However, [objects] although each of above-mentioned JP,S54-38348,A, JP,S54-38349,A, and resin composition objects given in the Europe patent No. 311,909 Description is the useful flame-retardant-resin material which does not use a halogenated compound Since fluid low polyphenylene ether was made into the subject, there was a problem that the moldability of a resin composition object was inferior.

[0005] Moreover, (b) unsaturated polyester, a (b) metal hydroxide, (c) red phosphorus or phosphorus compounds, and the resin composition object that consists of a (d) molybdenum compound are indicated by JP,S55-161845,A. However, although the resin composition object of ** et al. and this gazette is excellent in fire retardancy, since the metal hydroxide is used so much, shock resistance is low.

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[0006] Furthermore, Macromolecules It is indicated by 1980 and 13,280-288 by adding a chromium metal-powder object in polypropylene that incombustible material improves. However, fire retardancy effective in styrene resin only by only adding a chromium metal powder cannot be attained.

[0007]

[Problem to be solved by the invention] This invention aims at there being no above troubles, namely, offering the styrene resin composition which can reduce the conventional flame retarders substantially and has advanced fire retardancy and shock resistance in view of such the actual condition.

[0008]

[Means for solving problem] This invention persons receive conventional (A) rubber denaturation styrene resin, (B) polyphenylene ether, the (D) organic phosphorous compound, and (E) triazine frame content compound, as a result of considering a fire-resistant improvement of styrene resin wholeheartedly. A header and this invention were reached [that it becomes possible to raise fire retardancy by leaps and bounds and], holding shock resistance, even if it reduced the conventional flame retarders substantially to the surprising thing by combining a metal-containing fire retardancy catalyst.

[0009] This invention Namely, (A) rubber denaturation styrene resin, (B) polyphenylene ether, (C) Offer the metal-containing fire retardancy catalyst which are a metal oxide and/or a metal powder, the (D) organic phosphorous compound, and the styrene system shock resistance resin composition object which has the outstanding fire retardancy which consists of a (E) triazine frame content compound. This invention is explained in detail hereafter.

[0010] The resin composition object of this invention consists of (A) rubber denaturation styrene resin, (B) polyphenylene ether, (C) metal-containing fire retardancy catalyst, a (D) organic phosphorous compound, and a (E) triazine frame content compound, and even if it lacks the any, it cannot attain the object of invention. The above-mentioned (A) component bears the principal component of a molding resin composition, and the role of nothing and intensity maintenance of mold goods [the above-mentioned (D) component] (E) It is a component for giving fire retardancy with a component to the (A) component, and the above (B) and the component of (C) are components for heightening further the fire-resistant grant effect of (D) and the component of (E) further.

[0011] Here, the metal oxide in (C) metal-containing fire retardancy catalyst acts as a dehydrogenation catalyst, and oneself, a metal powder serves as a metal oxide and promotes carbonization of a constituent with combination with (B) polyphenylene ether while it acts as a scavenger of the OH and the radical generated at the time of fire retardancy. [styrene resin / of the above-mentioned (A) component / rubber denaturation] The polymer which a rubber-like polymer distributes in the shape of a particle in the matrix which consists of a vinyl aromatic series system polymer is said. The vinyl monomer in which this and copolymerization are possible is added an aromatic vinyl monomer and if needed under existence of a rubber-like polymer, and monomer mixture is obtained a well-known bulk polymerization, a massive suspension polymerization, solution polymerization, or by carrying out an emulsion polymerization.

[0012] As an example of such resin, high impact polystyrene, ABS plastics (acrylonitrile Butadiene Styrene), AAS resin (acrylonitrile acrylic rubber styrene copolymer), AES resin (acrylonitrile ethylene-propylene rubber styrene copolymer), etc. are mentioned. Here, said rubber-like polymer requires that glass transition temperature (T_g) should be less than -30 degree C, and if -30 degrees C is exceeded, shock resistance will fall.

[0013] As an example of such a rubber-like polymer, polybutadiene, poly (styrene butadiene), The saturation rubber which hydrogenated diene system rubber and the above-mentioned diene rubber, such as poly (acrylonitrile butadiene), Acrylic rubber, such as polyisoprene rubber, chloroprene rubber, and polyacrylic acid butyl, an ethylene propylene diene monomer ternary polymerization object (EPDM), etc. can be mentioned, and especially diene system rubber is desirable.

[0014] [aromatic vinyl monomer / of the essential ingredient in the monomer mixture in which graft polymerization is possible] For example, although it is styrene, alpha-methylstyrene, PARAME chill styrene, p-chloro styrene, p-bromostyrene, 2, 4, and 5-TORIBUROMO styrene etc. and styrene is the most desirable, you may copolymerize an aromatic vinyl monomer besides the above for styrene to a subject.

[0015] Moreover, more than a kind can introduce the monomer component which can be copolymerized in an aromatic vinyl monomer if needed as a component of rubber denaturation styrene resin. When there is the need of raising oil resistance, unsaturated nitrile monomers, such as acrylonitrile and a methacrylonitrile, can be used. And when there is the need of reducing the melt viscosity at the time of a blend, the acrylic ester which a carbon number becomes from the alkyl group of 1-8 can be used. Furthermore, when there is the need of raising the thermal resistance of a polymer composition further, you may copolymerize monomers, such as an acrylic acid, a methacrylic acid, a maleic anhydride, and N-substitution maleimide. The content of the above-mentioned vinyl aromatic series monomer and the vinyl monomer which can be copolymerized occupied in monomer mixture is 0

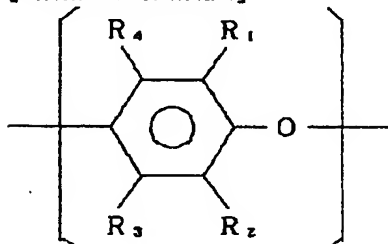
to 40 % of the weight.

[0016] The rubber-like polymer in rubber denaturation styrene resin of this invention is desirable, 5 to 80 % of the weight and the monomer mixture in which it is still more desirable and 10 to 50 % of the weight and graft polymerization are possible are desirable, and 95 to 20 % of the weight is in 90 to 50% of the weight of the range still more preferably. It becomes impossible to maintain balance shock-proof [of this polymer composition made into the object if out of range], and rigid. Furthermore, as for the rubber particle diameter of a styrene system polymer, 0.1-5.0 micrometers is desirable, and 0.2-3.0 micrometers is especially suitable for it, the above — if out of range, the inclination for shock resistance to fall is produced.

[0017] the gay polymer which the polyphenylene ether (it calls for short Following PPE.) of the (B) component of this invention becomes from the joint unit shown by the following formula — and/or, a copolymerization object is.

[0018]

[Chemical formula 1]



[0019] However, R1, R2, R3, and R4 It is chosen from the group which consists of hydrogen, a hydrocarbon, or a substitution hydrocarbon group, respectively, and even if mutually the same, you may differ. As this concrete example of PPE, the copolymer of poly (2, 6-dimethyl 1, 4-phenylene ether), 2, and 6-dimethylphenol and 2, 3, and 6-TORIME chill phenol etc. is desirable, and poly (2, the 6-dimethyl 1, 4-phenylene ether) is desirable especially. This manufacture method in particular of PPE is not limited, and the complex of the cuprous salt according [for example,] to a method given in a U.S. Pat. No. 3,306,874 Description and an amine is used as a catalyst. For example, it can manufacture easily by carrying out the oxidation polymerization of the 2 and 6-xenol. It can manufacture easily by the method indicated in addition to this to a U.S. Pat. No. 3,306,875 Description, a U.S. Pat. No. 3,257,357 Description, a U.S. Pat. No. 3,257,358 Description and JP,S52-17880,B, and JP,S50-51197,A. As for the reduced viscosity (0.5g/dl, a chloro film solution, 30-degree-C measurement) of the above PPE used in this invention, it is desirable that it is in the range of 0.20 - 0.70 dl/g, and it is more desirable that it is in the range of 0.30 - 0.60 dl/g. As a means for satisfying the above-mentioned requirements about the reduced viscosity of PPE, adjustment of the amount of catalysts in the case of said manufacture of PPE etc. can be mentioned.

[0020] [catalyst / moreover, / of the (C) component of this invention / metal-containing fire retardancy] Are a metal oxide and/or a metal powder and [the above-mentioned metal oxide] An aluminum oxide, an iron oxide, titanium oxide, manganese oxide, a zinc oxide, It is simple substances or those complex (alloy), such as molybdenum oxide, cobalt oxide, a bismuth oxide, chrome oxide, tin oxide, antimony oxide, nickel oxide, copper oxide, and tungstic oxide, and especially molybdenum oxide (MO O2) and chrome oxide (Cr 2O3) are desirable. And the metal powders in the (C) component are simple substances or those complex (alloy), such as aluminum, iron, titanium, manganese, zinc, molybdenum, cobalt, a bismuth, chromium, nickel, copper, a tungsten, tin, and antimony, and especially its chromium powder (Cr) is desirable.

[0021] As for the particle diameter of the metal-containing fire retardancy catalyst of this invention, 0.01 micrometer - 100 micrometers are desirable. If a particle diameter exceeds 100 micrometers, surface area will decrease, fire retardancy will fall and, on the other hand, fire retardancy will fall secondary condensation at less than 0.01 micrometer for poor lifting distribution. Moreover, in order to raise compatibility with styrene resin, you may carry out surface treatment by the higher fatty acid, a polysiloxane, etc.

[0022] Furthermore, as an organic phosphorous compound of the (D) component of this invention, a phosphine, phosphine oxide, a BIHOSU fin, phosphonium salt, phosphinate, phosphoric ester, phosphite, etc. can be mentioned. More specifically A methyl neopentyl FOSU fight, pentaerythritoldiethyldiphosphite, Methyl neopentyl FOSUFONETO, phenyl neopentyl phosphate, Pentaerythritol JIFENIRUJI phosphate, JISHIKURO pentyl HAIPOJI phosphate, Dineopentyl hypophosphite, a phenyl pyrocatechol FOSU fight, ethyl pyrocatechol phosphate, JIPIRO catechol HAIPOJI phosphate, etc. can be mentioned.

[0023] And a melamine is the most desirable, although the triazine frame content compound of the (E) component

of this invention can act as a fire-resistant assistant of an organic phosphorous compound and a melamine, SAKUSHINO guanamine, AJIPO guanamine, methyl GURUTARO guanamine, etc. can be mentioned as the example. In the resin composition object of this invention, although (A) rubber denaturation styrene resin and (B) polyphenylene ether form a resinous principle, the rate of the (B) component occupied in the 100 weight sections of the above-mentioned resinous principle has the desirable range of 10 – 30 weight section. (B) There are few amounts of carbonaceous residue and the fire retardancy of under 10 weight sections is not enough as a component, and if 30 weight sections are exceeded, a fluidity falls and it is not desirable. (B) The more desirable range of a component is 10 – 25 weight section.

[0024] Next, as for the resin composition object of this invention, it is desirable that 1 – 30 weight section has (C) metal-containing fire retardancy catalyst in the range of 5 – 30 weight section, and 1 – 30 weight section and (E) triazine frame content compound have the (D) organic phosphorous compound in it to a total of 100 weight sections of the component of (A) and (B). If it deviates from the above-mentioned range here, fire retardancy or shock resistance falls and is not desirable.

[0025] [a polymer composition] although the polymer composition of this invention is obtained by carrying out melting kneading of each above-mentioned polymer with a commercial single screw extruder or a commercial twin screw extruder etc., for example etc. Lubricant, such as antioxidants, such as BHT, an ultraviolet ray absorbent, a tin system thermostabilizer, stearin acid, and zinc stearate, a bulking agent, reinforcing materials, a color, a pigment, etc. can be added if needed in that case. Thus, fire-resistant and shock-proof outstanding mold goods are obtained injection molding or by carrying out extrusion molding in the constituent of obtained this invention.

[0026]

[Working example] Hereafter, although an example explains this invention to details further, thereby, this invention does not receive a limit at all. In addition, measurement in an example and a comparative example was performed using the following methods or measuring equipment.

(1) Fire retardancy;

VB (Vertical Burning) law based on UL-94 estimated. (1/8-inch test piece)

(2) Izod impactive strength;

It measured at 23 degrees C by the method based on ASTM-D256. (V notch, 1/8-inch test piece)

[0027]

[An example 1]

(**) The polymerization undiluted solution of the manufacture following presentation of rubber denaturation styrene resin (HIPS) was adjusted.

Polybutadiene rubber The 8.0 weight sections (made by Asahi Chemical Industry Co., Ltd. NF-35A)

Styrene The 77.0 weight sections Ethylbenzene The 15.0 weight sections A alpha-methylstyrene dimer The 0.06 weight section Stearyl 3 -(3,5-di-tertiary-butyl 0.10 weight section -4-hydroxyphenyl)- It polymerized by the propionate following ** by sending the above-mentioned polymerization undiluted solution continuously to the multistage type reaction machine equipped with the stirring rod. The rubber grain child's weighted mean particle diameter adjusted polymerization temperature and the number of churning so that the solid content concentration of 2.3 microns and the last reaction machine appearance might become 80 % of the weight. It led to the devolatilizer of polymerization liquid succeedingly, and rubber denaturation vinyl aromatic series resin (HIPS) of 10 % of the weight of rubber contents was obtained. As a result of analyzing the obtained rubber denaturation vinyl aromatic series resin, as for the swelling index of the gel component, the reduced viscosity of the gel content of 12.5 and a matrix portion was 0.75 dl/g 32% of the weight.

(**) It has the manufacture oxygen blowing-in mouth of polyphenylene ether (PPE) at the reaction machine bottom. After nitrogen replaces enough the interior of the reaction machine made from stainless steel which has a coil for cooling, and a churning wing with the interior, bromination — 2,6-xyleneol 8.75kg was dissolved in the mixed solvent of 54.8g of the 2nd copper, 1110g of G n butylamine and 20l. of toluene, and 4l. of 16l. of n-butanols methanols, and it taught the reaction machine. Oxygen was continuously blown into the interior of a reaction opportunity, agitating, and the polymerization was performed for 180 minutes, controlling an internal temperature at 30 degrees C. The ** exception carried out the polymer which deposited after the end of a polymerization, a methanol / hydrochloric-acid mixed liquor was added, and the residual catalyst in polymer was decomposed, after washing enough using a methanol further, it dried, and powdered PPE was obtained. Reduced viscosity was 0.55 dl/g.

(**) As a metal-containing fire retardancy catalyst metal oxide, commercial molybdenum dioxide powder (MO O2) (made by SOEKAWA CHEMICAL Co., Ltd.) was used. (MO O2 is called below.)

(**) As an organic phosphorous compound organic phosphorous compound, commercial triphenyl phosphate (made in large 8 Chemical-industry Place) was used. (Following TPP is called.)

(**) As a triazine frame content compound triazine frame content compound, the commercial melamine (product made from Wako Pure Chem Industry) was used (Following ML is called).

(**) Adjustment of a constituent, and assessment above-mentioned HIPS/PPE/M0 O2 / TPP/ML were mechanically mixed by the ratio of 77/23/4/12/12 by the bulk density, and it fused for 5 minutes using the Oriental energy machine factory lab PURASUTO mill at the melting temperature rotational frequency of 50rpm of 230 degrees C. Thus, the test piece of 1/8-inch thickness was produced with hot press from the obtained polymer composition, and fire retardancy and assessment of Izod impact strength were performed. The result is shown in a table 1.

[0028]

[An example 2] In the example 1, the same experiment as an example 1 was repeated except using chrome oxide (Cr 2O3) [(Nippon Chemical Industrial Co., Ltd. make, trade name KUROMEKKUSU A-1, particle diameter of 0.2 micrometer) (the following Cr 2O3 being called)] as a metal-containing catalyst. The result is shown in a table 1.

[0029]

[An example 3] In the example 1, the same experiment as an example 1 was repeated except using chromium metal-powder (Cr)[(TOSOH CORP. make and trade name Met Cr St-p325, particle diameter of 44 micrometers) (Cr being called)] as a metal-containing catalyst. The result is shown in a table 1.

[0030]

[A comparative example 1] In an example 1, it is M0 O2. It did not add and also the same experiment as an example 1 was repeated. The result is shown in a table 1.

[0031]

[A comparative example 2] In the example 1, TPP was not added and also the same experiment as an example 1 was repeated. The result is shown in a table 1.

[0032]

[A comparative example 3] In the example 1, ML was not added and also the same experiment as an example 1 was repeated. The result is shown in a table 1.

[0033]

[A comparative example 4] In the example 1, the same experiment as an example 1 was repeated except changing into HIPS100 the resinous principle 100 which becomes 77/23 of HIPS/PPE of bulk densities. The result is shown in a table 1.

[0034]

[Table 1]

例		樹脂組成物（重量比）					アイゾット衝撃強さ (kg-cm/cm)	UL-94-VB法による燃焼テスト		
		高変性 スチレン 系樹脂 (HIPS)	ポリフェ ニレンエ ーテル (PPE)	含金属 難燃 触媒	有機リ ン化合 物 *1 (TPP)	トリアジ ン骨格含 有化合物 (ML) *2		消炎 時間 (秒)	火種 の 滴下	判定
実施例	1	77	23	4 (Mo O ₂)	12	12	6.3	4.5	無	V-0
	2	77	23	4 (Cr ₂ O ₃)	12	12	6.3	5.0	無	V-0
	3	77	23	4 (Cr)	12	12	7.2	4.0	無	V-0
比較例	1	77	23	0	12	12	7.1	6.0	無	V-1
	2	77	23	4 (Mo O ₂)	0	12	4.4	35.3	有	*3 HB
	3	77	23	4 (Mo O ₂)	12	0	13.2	11.0	無	V-1
	4	100	0	4 (Mo O ₂)	12	12	3.7	30.0	有	*3 HB

*1) TPP: トリフェニルフォスフェート。

*2) ML: メラミン。

*3) HB: UL-94、V-0、V-1、V-2 のいずれの燃焼
ランクにも達していないことを示す。

035]

ffect of the Invention] Even if the constituent of this invention reduces the conventional flame retarders
bstantially, it is a styrene resin composition which had advanced fire retardancy and shock resistance. This
nstituent is suitable for household appliance parts, OA equipment parts, etc., and the role played in the
ustrial world is large.

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